ELECTROCHEMICAL INVESTIGATIONS ON SEMICONDUCTING METAL SULFIDES NANOPARTICLES BY USING SINGLE SOURCE PRECURSOR FOR ENERGY STORAGE APPLICATION

SYNOPSIS

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SAMBATHKUMAR C
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ANAND NAGAR, KRISHNANKOIL - 626 126

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I. Introduction

In the 21st century, the portable electronic devices such as smart phones, activity trackers, laptop, cameras, and smart watches are changing the day to day life styles globally. The increasing energy consumption for smart electronics devices has much required and it is satisfying through the energy storage devices [1]. Energy storage devices can be followed into several categories including chemical energy storage with conversion devices (e.g. Fuel cell, water splitting), mechanical energy storage (e.g. flywheels), Thermo-chemical energy storage (e.g. solar hydrogen, heat storage, solar thermal energy), electrical energy storage (e.g. physical capacitors) and electrochemical energy storage (e.g. pseudocapacitors, electrical double layer capacitors, batteries) [2]. Besides, the sustainable post-fossil-fuels are useful to construct the energy storage devices [1–3].

Furthermore, the electrochemical energy storage devices like batteries and supercapacitors are developed in research laboratories and industries. In addition, the supercapacitor and batteries are differing from the charge storage mechanism based on their materials suited structure. However, the batteries are designed to provide high energy density by storing charge in the bulk electrode via redox reactions. Supercapacitors are providing high power density and it is storing the charges based on the surface absorption and also faradaic reactions. Moreover, the supercapacitors has long life time (1,00,000 cycles) compared to battery (from 500 to 10,000 cycles). Also, supercapacitor has provided high specific power (20000 W kg^{-1}) [4–5]. The electrochemical supercapacitor can be categorized into two types, such as pseudocapacitors (PCs) and electric double layer capacitors (EDLCs). The EDLCs are storing the charges via absorption and desorption of ions and PCs are storing the charges via faradaic reactions between the electrode and electrolyte [5–6].

Lithium-Ion Batteries (LIBs) can attain high specific energy (75–200 Wh/kg) through redox reactions on their electrodes but suffer from low specific power (0.1–1 kW/kg), which leads to decrease in its lifespan, long charging times and poor cycle stability compared to supercapacitors. It may explode upon overheating or overcharging [7–8]. Researches were conducted on a considerable scale to discover accessible and functional electrodes (electrically conductive and possess high electrochemically active surface area). AC has low specific capacitance (200–220 Fg^{-}

[1]) due to its inability to store charge through redox reaction. The most promising materials with a peculiar capacitance value (209 Fg^{-1}) is the hydrous ruthenium oxide, usually employed in pseudocapacitor. Due to the high cost, its commercialization is limited. While transition metal oxides and metal sulfides are remarkable high specific capacitance value, high yield and easily abundant [9–12]. Transition metal sulfides (TMS) have been considered promising alternative electrode materials for faradaic supercapacitors (FSs) applications. Indeed, the TMS have huge advantages whereas cost effective, excellent chemical stability, low electronegativity, easy availability, easy way to approaches, peculiar morphologies, and high surface area compared with their corresponding oxides or hydroxides. There is a more flexible structure related to the changed chemical bonds in TMSs after replacing oxygen (higher electronegativity) with sulfur (lower electronegativity), which could facilitate electrons transport and reduce band gap and thus achieve a better stability in long-term charge/discharge processes [13].

Besides, it is play an important role in the electrode material for electrochemical capacitors such as, high theoretical specific capacitance, high cycling stability, good electrical conductivity, outstanding pseudocapacitance behaviour in larger potential range [14]. Furthermore, offer conspicuous capacitance improvements obtained by TMSs controlling and adjusting their defects and also surface/interface under a small nanoscale. Their energy density improved certain degree, their electrical conductivity, volume expansion and indolent ion diffusion in the bulk phase has hindered their practical application [15]. In supercapacitor applications, various Metal Sulfides (MSs) are acting a major role as working electrode materials such as, CoS, Bi_2S_3, Fe_2S, CuS, etc [16-19]. Recently, MSs have gain major attention as electrode materials owing to their unique electrochemical properties, low cost, highly abundance, stress-free production and high theoretical capacitance value which makes them potential substitutes for noble metals in a range of fields with high effectiveness.

In recent years, various sulfur containing source complex molecules have been major employed for metal sulfide nanoparticles synthesis. In recent, very few reports are available by using metal complex (diethyldithiocarbamate) as single source precursor in metal sulfide NPs synthesis; from this method we can achieve different peculiar shaped nanoparticles like sheet, rod, spherical, cube, and flake with high

purity [20]. The single-source precursor is normally more secure, less expensive and steadier than the utilization of at least two precursors. In addition, the main purpose of the single source precursor methods were used to industrial scale synthesis, avoid extensive washing and complicated experimental conditions. It is assumed that, this technique is effortless and effective for the metal sulfide synthesis at low temperature. The focus will be on the use of metal complexes as single molecule precursors to synthesize surface-passivated semiconductor nanoparticles [21].

In the present investigation, metal complexes like nickel diethyldithiocarbamate ($Ni[DTC]_2$), bismuth diethyldithiocarbamate ($Bi[DTC]_3$), cobalt diethyldithiocarbamate ($Co[DTC]_2$), copper diethyldithiocarbamate ($Cu[DTC]_2$), cadmium diethyldithiocarbamate ($Cd[DTC]_2$), were developed and employed as single source precursor for the synthesis of Ni_9S_8, Bi_2S_3, Co_9S_8, CuS and CdS using an solvothermal reflex method at low temperature. All the prepared material are characterized and have been studied its electrochemical performance through cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy analysis. Thus, the present study is also suggested that the developed metal sulfides as electrode material for supercapacitor application.

II. LITERATURE SURVEY

Application with high specific capacitances of 348 Fg^{-1} at current density of 1 Ag^{-1} (3-electrode system) using 6M KOH electrolyte solution was designed by Ashok Kumar [16]. It has reported that the hexagonal structured CoS material was synthesized by facile hydrothermal route at 180 ºC for 24 h. The prepared electrode material was a good cyclic performance of 98% capacitance after continuous 2000 charge-discharge cycles. Sonai Muthu et al. [22] has reported that influence of thiourea concentration on the CuS nanostructures as an electrode material by simple hydrothermal method at 130 ºC for 20 h and the material was obtained granular morphology. The changes in thiourea concentration greatly affected the physical and electro chemical features of CuS. The CuS electrode reported highest specific capacitance of 298 Fg^{-1} at 2 Ag^{-1} was obtained for copper sulfide nanoparticles prepared with 1:2 ratio of copper acetate and thiourea. It exhibits excellent cycling stability of 100% in 2 M KOH electrolyte. Liu et al. [17] has showed high electrochemical performance (233 Fg^{-1} at 1 Ag^{-1}) and good cycling stability in this research work with Bi_2S_3 electrodes using 6M KOH electrolyte. The hierarchal Bi_2S_3

nanoflowers were synthesized by a topotactic transformation route at 180 ºC for 24 h. Heydari et al. [23] has report a simple strategy for high-performance supercapacitors by building pseudocapacitive CuS nanosphers with nanoporous structures, nanosized walls (< 10 nm) and relatively large specific surface area of 65 m^2/g. This electrode demonstrates electrochemical performance including specific capacitance of 814 Fg^{-1} at 1 Ag^{-1}, and good cycling retention of 95.9% after 1000 charge-discharge cycles using 6M KOH electrolyte. The hydrothermal method (160 ºC for 24 h) was used for material synthesis then the result has nanosphers-like morphology with a hexagonal CuS phase. Moreover, Nisha et al. [24] has reports the synthesis and pseudocapacitor applications of 2D cadmium sulphide (CdS) nanosheets deposited on Ni foam via electrophoretic deposition method (80 ºC for 48 h). It is exhibited high electrochemical performance of 146 Fg^{-1} at ~~a~~ current density of 2 Ag^{-1} using 3M KOH electrolyte. In Xing et al. [25] reports, the octahedron-shaped CoS_2 crystal has been successfully prepared through a simple hydrothermal route without any surfactant or template. CoS_2 electrode shows typical pseudocapative properties with a specific capacitance of 236.5 Fg^{-1} at 1Ag^{-1}. Remarkably, it exhibits an excellent cycling stability at 2 Ag^{-1} with a loss of 7.4% in the specific capacitance after 2000 cycles in 2M KOH electrolyte. In addition, Peng [19] has reported that the developed CuS with different morphologies (plate-like, nanoparticle-like, sphere-like, and flower-like) via a simple low-temperature solvothermal approach (150 ºC for 24 h) without any surfactant or template. The specific capacitance of the flower-like CuS synthesized in glycerol can reach up to 597 Fg^{-1} at 1 Ag^{-1}. Meanwhile, it as exhibits a good cycling stability of 80% after 1000 cycles in 2M KOH electrolyte solution.

III. OBJECTIVES

The objectives of the present investigations are

- Synthesis of different metal sulfide nanoparticles (Ni_9S_8, Bi_2S_3, Co_9S_8. CuS and CdS) using Metal dithiocarbamate ($M[DTC]_2$) as single source precursor and hexadecylamine as capping agent via solvothermal method at low temperature.
- The thermal stability and phase transition of the prepared metal complex were investigate by TG-DTA analysis.
- The prepared materials will be used by various characterization techniques such as, XRD, FTIR, Raman, SEM and EDS with mapping, HR-TEM and XPS.

Besides, analysis their properties such as structural, Spectroscopic, morphological and elemental compositional behaviors.

- Electrochemical performances of the metal sulfides (Ni_9S_8, Bi_2S_3, Co_9S_8. CuS and CdS) modified working electrode materials were investigated for SCs application using 1M KOH aqueous electrolyte.
- The prepared metal sulfides NPs modified working electrodes were studied with cyclic voltammetry (CV), Charge-discharge characteristics (GCD), and electrochemical impedance spectroscopy (EIS) analysis. In addition, cyclic stability, retention and columbic efficiency of fabricated electrodes were investigated for energy storage applications (supercapacitor).
- Fabrication of Co_9S_8||AC and CuS||AC based asymmetric supercapacitor devices. The performance of asymmetric supercapacitor devices were studied by cyclic voltammetry, charge discharge analysis, electrochemical impedance spectroscopy analysis. The cyclic stability and retention of the device performance have been analysis.

IV. RESEARCH PROBLEM

As per fundamental requirements of electrode material to the energy storage needs to fast electron transport. The potential applications of metal oxide based SCs electrodes have limits of specific capacitance values, structural stability, corrosion, poor cyclic stability, and life span. Henceforth, to overcome these issues TMS with superior performances were proposed. TMSs have been widely investigated as pseudocapacitive electrode materials due to their rich oxidation states available for reversible redox reaction. In this regards, we have proceed different TMSs with evaluated superior electrochemical performances, good electronic conductivity, large surface area, high structural richness, cyclic stability and low resistivity properties as an electrode material for SCs. In order to achieve the objectives of this thesis, all possible experimental techniques, structural, spectroscopic and morphological analysis were done and discussed in detail. The detailed analysis of electrochemical performance might be achieved with the special emphasis on the SC power output.

V. ORGANIZATION OF THESIS

The research problem as stated above is designed as research work of this thesis as shown in flow chart of Figure 1. The research presented in this thesis showed

synthesizes and characterization of different TMSs nanoparticles based SC electrodes that possess higher specific capacitances with long life cycle. Along with the electrochemical studies, their analytical properties such as structural, morphological, spectroscopic and binding energies are also studied.

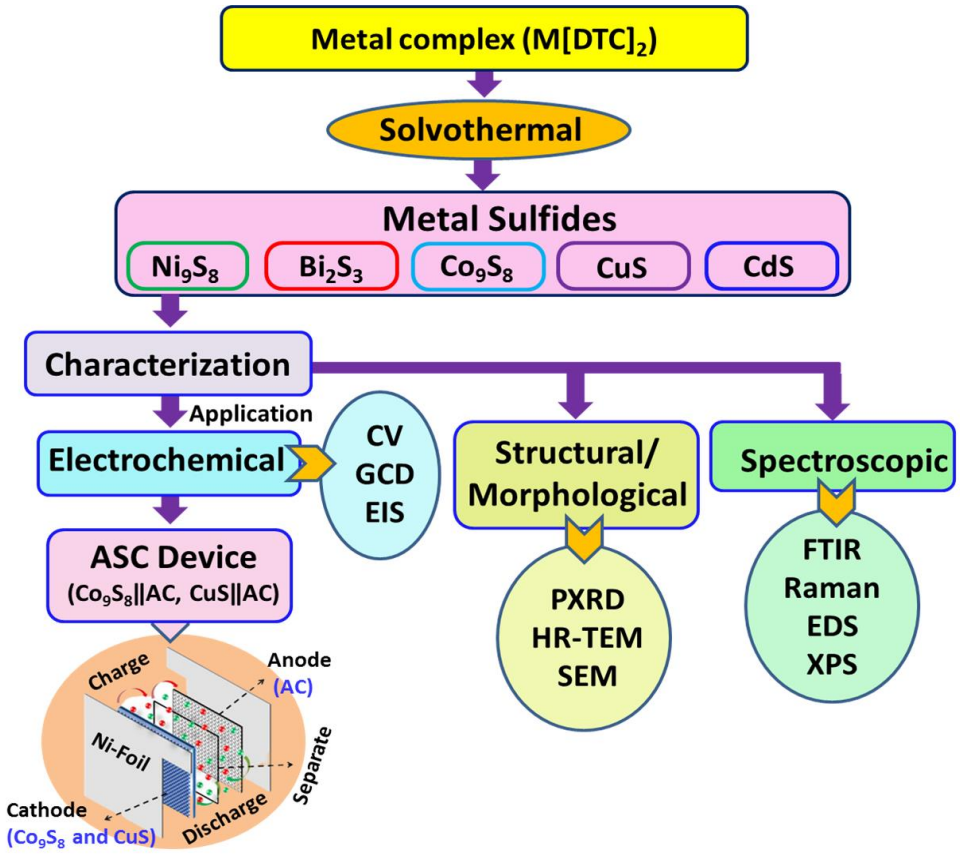

Figure 1: The schematic diagram shows material synthesis and characterization work flow

Chapter 1: Introduction about energy storage materials

Chapter 1 described about the introduction of the wide spread real-time applications of energy storage device needs and the necessities of developing new and alternative energy resources and energy storage devices. Energy storage and their conversion were playing an important role in our everyday life due to increasing interest of clean energy technologies. In this chapter, clearly states that the role of electrochemical energy storage devices and its importance in technological applications were deliberated. A detailed description of SCs and its types based on their reaction mechanism were highlighted. The components of various SCs and their requirements were discussed. Role of various transition metal sulfides and its nanostructures in PCs

were discussed. Along with these, metal sulfides synthesis form single source precursor and its benefits, limitations of metal sulfide NPs modified as working electrode were also presented.

Chapter 2: Literature survey

Chapter 2 deals with the detailed Literature survey about metal chalcogenides especially metal sulfide based energy storage supercapacitors electrode materials and their performances were summarized. Different types of synthesis techniques and its roles on the electrode materials efficiency were listed. The demerits of metal oxide usages as electrode materials were reviewed and the solutions to rectify those demerits were reviewed in detail. Based on the literature review, we identified the research gap which reduces the possibility of using prepared electrode materials in real time applications and the objective of the thesis work were framed. Based on the literature survey, the metal sulfide based electrode materials exhibit good electrochemical reaction and high performance supercapacitors. An outline of the scope of the present investigation is provided towards the end of this chapter.

Chapter 3: Materials and methods

This chapter described about the synthesize of metal complexes' ($M[DCT]_2$) (M = Ni, Bi, Co, Cu and Cd) by using sodium diethyldithiocarbamate precursor followed by metal sulfide nanoparticle synthesis by using ($M[DCT]_2$) via solvothermal techniques. In addition, clearly discussed about the metal sulfide NPs modified electrode fabrication for the electrochemical studies. Moreover, this chapter reveals the basic characterization and including TG-DTA, PXRD, FTIR, SEM, HR-TEM, EDS with mapping, XPS analysis and electrochemical workstation functions. The characterization results described the thermal stability of the metal complex, structural, spectroscopic, morphological, elemental analysis and electrochemical performance of the material. This chapter interconnected to the experimental studies and electrochemical performance of the material.

3.1 Synthesis of single source precursor (Metal complex-$M[DTC]_2$)

In the typical synthesis, 1:2 Mole of metal precursor [Metal (M):Ni, Bi, Co, Cu, and Cd] and $C_5H_{10}NNaS_2.3H_2O$ were separately dissolved in each 50 mL of DI water and ethanol respectively. The sodium diethyldithiocarbamate solution was drop wise added in metal precursor at cold condition (~4 °C) in meantime coloured metal

complex ($M[DTC]_2$) were formed and it was allowed to constant stir up to 1 h. Here, the sodium (Na) metal ions replaced by aimed metal ions and it is formed as metal diethyldithiocarbamate shown in the below Figure 2. Finally the product was collected using centrifuge machine and washed 3 times with DI water followed by ethanol respectively. The ($M[DTC]_2$) was dried overnight at 60 °C in hot air oven and stored in glass container for further use [20, 26] the same procedure were followed for all metal complex preparations.

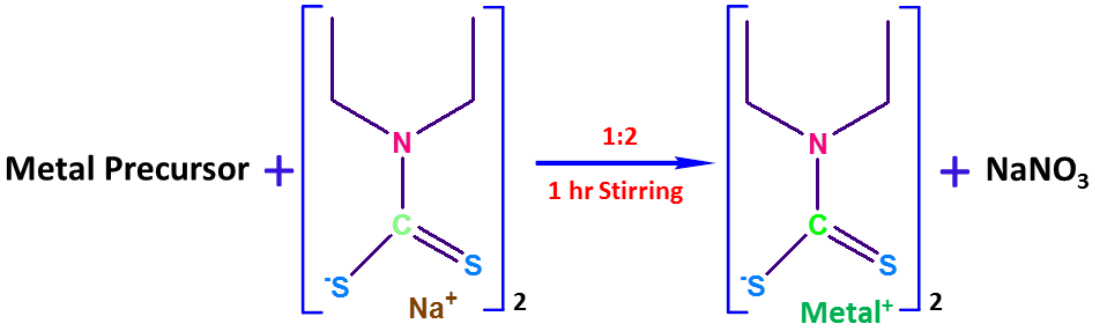

Figure 2: Synthesis of single source precursor ($M[DTC]_2$).

3.2 Synthesis method of the metal sulfide nanoparticles

In this work, all the metal sulfides were synthesized via solvothermal reflux method. An equal (1:1) weight ratio of ($M[DTC]_2$) complex and hexadecylamine (HDA) were dispersed in 100 mL of N, N- Dimethylformamide and homogenously mixed. The reactant solution transferred to solvothermal reflux setup and stirred under 120 °C reaction temperatures for 30 min and the coloured precipitation of metal sulfide (MS) were obtained, the final product was washed with methanol (CH_3OH) until remove the un-reacted/excess HDA. Then the as prepared metal sulfide was dried in an oven at 60 °C for 12 h [27]. Figure 3 shows the flow diagram of the MS NPs synthesis.

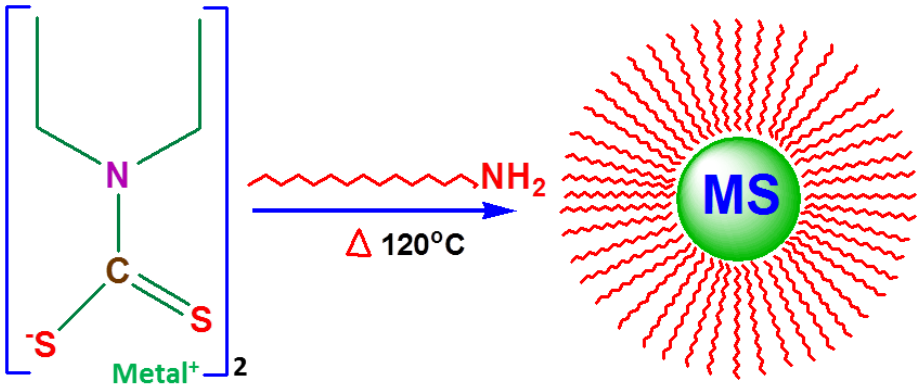

Figure 3: Schematic diagram of metal sulfide NPs form single source precursor.

Chapter 4: Results and discussion

Chapter 4.1 deals with nickel sulfide nanoparticles modified electrode material from single-source precursor for energy storage supercapacitor application. Herein, Nickel (II) Diethyldithiocarbamate was used as single-source precursor for Nickel Sulfide (Ni_9S_8) two-dimensional (2D) nanosheets (NSs) preparation and hexadecylamine as shape directing agent via simple solvothermal techniques. The orthorhombic structure of Ni_9S_8 NSs was confirmed by X-ray diffraction (XRD) pattern. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed that as-prepared Ni_9S_8 nanoparticles possess sheet-like morphology. Besides, the thermal stability of $Ni[DTC]_2$ complex was studied by TG-DTA analysis. The electrochemical properties of Ni_9S_8 NSs were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) techniques. From the charge-discharge study of Ni_9S_8 NSs, a high specific capacitance of 281 Fg^{-1} was obtained at a current density of 1 Ag^{-1} and up to 82% retentivity was achieved after 5000 cycles. These results are discussed in detail.

Chapter 4.2 deals with electrochemical investigation of Bi_2S_3 nanoparticles synthesis using bismuth diethyldithiocarbamate as single source antecedent for energy storage application. The synthesized Bi_2S_3 NPs were affirmed by thermal, structural and morphological with elemental analysis. The electrochemical performances were investigated by CV, GCD, and EIS analysis with Bi_2S_3 NPs modified working electrode in 1M KOH electrolyte. It reveals that, exhibit redox behavior from CV analysis, the charge-discharge analysis was examined by the GCD and electrical conductivity of the sample was confirmed by EIS studies. Bi_2S_3 NPs exhibit excellent supercapacitor behavior with value of the specific capacitance 470 Fg^{-1} at current density 0.5 Ag^{-1} and the retentivity of 74.3% after 5000 cycles.

Chapter 4.3 explained about electrochemical exploration of cobalt sulfide nanoparticles synthesis using cobalt diethyldithiocarbamate as single source precursor for asymmetric supercapacitor device. The cobalt sulfide (Co_9S_8) nanoparticles (NPs) have been synthesized by the solvothermal techniques by utilizing cobalt diethyldithiocarbamate ($Co[DTC]_2$) as single-source precursor and hexadecylamine (HDA) as shape directing agent. As-prepared Co_9S_8 NPs were characterized with structural, morphological, thermal, spectroscopic and surface analysis using PXRD,

TEM, SEM-EDS, TG/DTA, FTIR, Raman and XPS studies respectively. The electrochemical performances were investigated by CV, GCD, and EIS analysis with Co_9S_8 NPs modified working electrode in 1M KOH electrolyte. The Co_9S_8 NPs modified electrode delivered excellent specific capacitances of 502 Fg^{-1} at current densities of 1 Ag^{-1}. The capacitance retention of Co_9S_8 NPs modified electrodes was found to be 89.3 % after 5000 cycles. Furthermore, asymmetric supercapacitor (ASC) device assembled with cathode and anode materials delivers a high energy density of 15.47 Wh kg^{-1} with power density of 1274.9 W kg^{-1}.

Chapter 4.4 discussed about electrochemical exploration on copper sulfide nanocubes synthesis by using single source precursor for enhanced asymmetric supercapacitor device. This metal chalcogenides based CuS nanocubes (NCs) were synthesized at low temperature by the solvothermal method using copper diethyldithiocarbamate ($Cu[DTC]_2$) as a single-source precursor in the presence of HDA as shape directing agent. As-prepared CuS NCs were confirmed with thermal, structural, vibrational and morphology with elemental studies. Further, the electrochemical behaviors of CuS NCs modified working electrode were examined in 1M KOH electrolyte. It exhibits notable specific capacitance of 1472.3 Fg^{-1} at 1 Ag^{-1} were obtained with excellent capacitive retention up to 93.6 % after 5000 charge-discharge cycles at the current density of 10 Ag^{-1}. Besides, the two electrode asymmetric supercapacitor (ASC) device was constructed and it exhibits the Csp of 54 Fg^{-1} at 3 Ag^{-1}. Even after 5000 cycles at 7 Ag^{-1} of current density, the ASC device was able to retain internal capacitance retention of 91.2 % due to its high energy density of 21.68 Wh kg^{-1} and power density of 1272.92 W kg^{-1}. After 5000 cycle's electrochemical evaluation of CuS NCs modified electrode were analyzed. The results are discussed.

Chapter 4.5 deals with Enhanced electrochemical performance of synthesized spherical shaped sub-10 CdS nanoparticles using single source precursor as an electrode material for energy storage application. In order to develop supercapacitors device with large scale-direct synthesis, high efficient and cost-effective materials have attracted considerable attention. Hence in this approach, sub-10 cadmium sulfide (sub-10 CdS) nanoparticles (NPs) have been successfully synthesized by solvothermal method at low temperature using ($Cd[DTC]_2$) as single source precursor and HDA as

shape directing agent. The prepared material was confirmed by structural, spectral, morphological, and elemental compositional analysis using variety of analytical tools. In addition, the electrochemical performance of the sub-10 CdS working electrode material was carried out via three electrode configurations in 1M KOH aqueous electrolyte. The resulting CdS electrode material delivering the notable specific capacitance of 456.3 Fg^{-1} at current density of 0.5 Ag^{-1} was estimated from GCD analysis. Likewise, the CdS modified working electrode only 8.8% loss in the material stability even after 5000 GCD cycles and the results are discussed.

Chapter 5: Summary and conclusion

This chapter reveals overall works with consolidates experimental results of chapter-4. Different metal sulfide nanoparticle (Ni_9S_8, Bi_2S_3, Co_9S_8, CuS and CdS) are synthesis by solvothermal method at low temperature using ($M[DTC]_2$) as single source precursor with long chain amine (HDA) as capping and shape directing agent. The prepared nanomaterials are subjected to various characterizations such as, TGA, XRD, FT-IR, Raman, SEM, HR-TEM, EDX and electrochemical analysis. By analyzing results and properties such as structural, spectroscopic, morphological behaviors were understood. The metal sulfide NPs modified working electrodes were utilized for electrochemical studies by cyclic voltammetry, Charge-discharge characteristics, and electrochemical impedance spectroscopy analysis. In addition, cyclic stability, retention and columbic efficiency of fabricated electrodes were investigated for supercapacitor applications. Based on the results, the prepared copper sulfide possessed superior electrochemical performances when compared with our prepared other TMSs. The overall summary of the results and analysis presented. Finally, the conclusion arrived from overall work of the thesis was discussed and compared. Also, the future extension of this thesis work was also stated in thesis.

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